CHARACTERIZATION OF CHEMICAL SPECIES IN COAL LIQUIDS USING AUTOMATED

SIZE EXCLUSION CHROMATOGRAPHY - GAS CHROMATOGRAPHY (SEC-GC)

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Introduction

Both size exclusion chromatography (SEC) and distillation are used to characterize species based on molecular weights which are determined indirectly either from SEC separation pattern (molecular size separation) (1-6) or from an ASTM distillation pattern. Boiling points can be used to estimate the molecular weight of the species but it is inadequate for chemical species characterization. The molecular separation by SEC is a powerful tool for determining molecular weights of polymers of known chemical structure. Although knowledge about the chemical structure of the component species are essential for the successful use of SEC,(5) it has certain advantages over distillations. SEC separations are less time consuming and can be used for both volatile and nonvolatile materials. Due to its simplicity, distillation is the most popular technique used for large and small separations and for the characterization of hydrocarbon fluids such as petroleum crudes, synthetic crudes, coal liquids and their refinery products. The performance of distillation cuts such as gasoline, kerosene and various lubricants are monitored and blended for standardizing performance rather than using the chemical composition for predicting the performance.

The high efficiency gel columns packed with 5μm particles have increased the efficiency and decreased the analysis time of size exclusion chromatography (SEC). Since relatively large samples can be separated in a time as short as 20 minutes, SEC can be used as a preliminary separation technique prior to other analytical techniques such as gas chromatography (GC) and gas chromatography-mass spectroscopy (GC-MS). Such SEC separation of coal liquids, petroleum crudes and their distillation cuts into four or five fractions, followed by the analysis of the SEC fractions by GC and GC-MS have been reported elsewhere (7-21). The fraction collection and concentration of fractions were performed manually. This procedures was inefficient, and susceptible to human error. The Automated fraction collection followed by injection of the fraction into the GC reduces analysis time, and offers and option for collecting a desired number of fractions at predetermined time intervals.

The SEC separates coal liquids into fractions containing species with similar linear molecular sizes. Since similar molecular size species in coal liquid happened to have similar functionalities, the size separation enables the separation of fractions containing similar chemical species. When tetrahydrofuran (THF) is used as the mobil phase the coal liquid can be separated into four fractions containing heavy nonvolatiles, long chain alkanes mixed with light nonvolatile, phenols and aromatics.

When the number of fractions are increased, less complex chromatograms with fewer peaks are obtained. The results of SEC-GC analysis of coal liquids indicate that the coal liquids are composed of a very large number of species but with similar structural blocks and functionalgroups. Lumping of similar components into four distinct groups such as nonvolatiles, alkanes (nonaromatic hydrocarbons), alkylated phenols and aromatics is seen as practical means of characterizing coal liquids.

In petroleum refinery industry the composition of distillation cuts are plotted versus distillation temperature. A similar technique is used for lumping of chemical species in coal liquid where the chemical composition is plotted versus elution volume (i.e. decreasing molecular size). In the SEC-GC set-up, the gas chromatograph can be visualized as a detector for SEC effluents. The GC out-put is used to determine the composition of SEC efficients. The instrumentation, SEC-GC analysis and chemical lumping of coal liquids are presented in this paper.

Experimental

A western Kentucky synthoil and lignite derived recycle solvents from the Energy Research Center, University of North Dakota were the samples used for the analysis. Dry, additive-free tetrahydrofuran (THF) under helium atmosphere was used for preparing sample solutions and as the mobile phase in the size exclusion chromatograph (SEC). Although the synthoil could be injected without dilution, a 50% solution was preferred in order to reduce possible peak spreading and tailing. Since the recycle solvents were very viscous, 25% solutions were used. All the solutions were filtered through 0.5 μm Millipore filters using modest heat (but not high enough to boil THF) from a hot air gun and 30 psi nitrogen pressure.

The instrumentation included a liquid chromatograph (LC, Waters ALC/SEC Model 202) equipped with a 60 cm, 5μm 100 Å PL gel column (Polymer Laboratories) and a refractive index detector (Waters Model R401) a Varian Chromatographic system (GC, VISTA 44) equipped with a 30 meter x 0.32 mm ID DB-5 capillary column (bonded phase fused silica column manufactured by J&W Scientific Co.) an autosampler (Varian 8000), a flame ionization detector (FID) and a nitrogen specific detector (thermionic ion specific - TSD) and a microcomputer system (IBM CS 9000) with 1000 K bytes RAM and dual 8" floppy disc drives for collecting raw chromatographic data.

The continuous sample separations on the gel column followed by the GC analysis of selected fractions was achieved by the operation of two sixport valves and a 34 port valve (All from Valco Instrument Company) as illustrated in Fig. 1. Sample injection into the LC was performed by a sixport valve (V_1) with a 2 ml sample loop and fitted with a syringe-needleport for variable sample size injection. The combined operation of another sixport switching valve and the 34 port valve (V_3) with 16 sample loops (100 μl) enabled the linking of the liquid chromatograph with the autosampler of the gas chromatograph. The autosampler was modified to handle 100 μl samples directly from the fraction collection loops of V_3. When V_2 was turned clockwise, it kept V_3 in line of LC effluents so that the fractions of separated sample could be collected and also the autosampler was bypassed. V_2 at its counter clockwise position kept V_3 in line with the autosampler for sample injection but bypassed the LC stream. Generally 0.1 μl sample size was used for GC analysis. The real time monitoring of the GC was possible on both Varian and IBM systems and the raw chromatographic data were stored on the 8" floppy discs. The fraction collection, sample injection into the GC as well as the data collection was performed by the integrated system composed of a Varian Automation System (VISTA 401) and the IBM microcomputer (CS 9000). For each sample injection into the SEC column, up to 16 fractions were collected and analyzed by the GC using appropriate gas chromatographic programs stored in the memory without any manual interaction.

Results and Discussion

The sample size recommended by column manufacturers for size exclusion chromato-
graphy is less than 1 mg in 10µls for good analytical separations. Increasing the
sample size can cause increase in peak width as well as loss of resolution. The
effect of sample size is demonstrated in Figure 10. Currently the gel columns are
available with high plate counts and high sample loading capacity. Larger smaples can
be loaded with some peak broadening which can be tolerated. When a sample like coal
liquid which is composed of a very large number of components, the sample sizes with
respect to individual species are small. Even overloading of the column with a large
coal liquid sample can give good separation of most species in coal liquid. Straight
chain alkanes are the one group of species which are present in relatively large
concentrations. The effect of coal liquid sample size is illustrated in Figure 11.
When the concentration of alkanes in the sample is small only few alkane peaks are
present in the gc of 0.1 µl SEC effluent. As the alkane concentration is increased
the peak spreading causes the several alkanes to spread into the 0.1µl fracation
analysed for the next interval. When the sample size is increased the peak intensi-
ties due to individual alkane do not increase proportionally but larger number of
alkanes are observed in the 0.1µl effluent "window". The overloading has a positive
effect on SEC fraction collection intervals. The smaller samples need frequent
intervals of fraction collection for GC analysis to identify all the components.
When the sample size is increased the column overloading will cause the species to
spread into a wider range and the fraction collection interval time can be increased.

The recycled solvent produced from Wyodak coal is selected to illustrate the
chemcial species in coal liquids using SEC-GC. A large sample size is selected and
the SEC column is overloaded with respect to alkanes. The gas chromatograms similar
to those in Figure 8 were obtained. The raw data from a blank run, where 0.1µl THF
was injected with out any coal liquid species, were subtracted from each raw data
using a base subtraction program, to obtain the reconstructed, gas chromatograms as
shown in Figure 12. Each of the 12 GC's represents the analysis SEC fraction: (see
Figure 7b for SEC separation Wyodak recycle solvent). Once question which arise at
this point is how much overlapping of species is there between the species found in
two 0.1µl SEC slices or how many of the gc peaks are not present in the previous
sample slice. In order to determine the new species and the species which are in
larger concentrations than the previous sample slice, the raw data of the previous
gas chromatogram is subratacted from that each GC raw data. (Only base line is
subtracted from the first one. First GC run data is subtracted from the second, the
second is subtracted from the third and so on). Figure 13 shows GC's with new peaks
and peaks which are larger than those in the previous GC.

When SEC-GC is used for coal liquid analysis, .1µl fractions of SEC effluents
are analyzed by GC to produce simpler gas chromatograms. Some of these gas chromato-
grams, for example the GC of longer alkanes, are composed chemically similar
components. The flame ionization detector (FID) response factor (based on mass), is
essentially the same for these larger alkanes. The total area counts of such gas
chromatograms excluding solvent peak, the area count of which represents the sample
volume (6.1µl), multiplied by the response factor will give the amount of alkanes
"lumped" together for the SEC fraction analyzed. Certain SEC fractions are composed
of two or more different chemical species due to the over lapping effect of similar
size species. For example the low boiling point alkanes mixed with the high boiling
point phenols where the linear molecular sizes of the species are similar. The
alkanes appear at low retention times whereas phenols appear at longer retention
times as expected. In these cases the area counts have to be lumped into two groups,
one for alkanes and another one for phenols. Each of these area counts multiplied by
the corresponding FID response factor indicate the amount of alkanes or phenols
present in the 0.1µl SEC fractions. All the sixteen or more GC of selected SEC .1µl
fractions of coal liquid or recycle solvents are individually analyzed for various
"lumped chemical" species in the fractions. Coal liquid sample separated by
distillation estimates the nonvolatile content. The SEC of nonvolatiles, volatiles

are reconstructed to show both in the same SEC output. These data along with SEC-GC data and used to reconstruct SEC of Wyodak coal derived recycle solvent as shown in Fig. 6.

The chemical lumping pattern shown in Fig. 6 is very similar to the plotting of distillation temperatures vs. composition, a technique commonly used in petroleum refining to simulate the composition of distillate as a function of temperature. Since SEC includes nonvolatiles, information on its size distribution is also shown. In each chemical lump the molecular weight decreases as SEC retention volume increases. The individual chemical lump has a SEC separation pattern similar to distillation temperature vs. molecular weight plot.

The chemical lump of alkanes is the simplest. Straight alkanes are distributed through out the range in a continuous pattern. Such a pattern does not exist for phenols and aromatics. Both of them have similar aromatic nucleus such as benzene, indan and naphthalene. The presence of hydroxy groups distinguishes the phenols from the aromatics. The alkyl side chains ranging mostly from C_1 to C_3 all attached to the simple aromatic nucleus result is larger molecules of phenols and aromatics. As the number of side chains increases, the number of isomers increase exponentially. The mass distribution of phenols and aromatics peaks at a certain molecular weight and then decreases at higher molecular weights. At the lower end of the mass distribution pattern, since a number of isomers possibly are smaller, the GC is well resolved and composed of larger well resolved peaks. At the higher molecular weight end, a very large number of isomers are possible in a small mass, the GC shows an upward shift in the base line which is due to a large number of species that are appearing unresolved. Since phenols have an inherent tendency for tailing, the large phenols are not at all resolved. In the case of large aromatics, the enormous number of isomers are appearing with quite a few peaks partially resolved.

The species which are unkown and have not been identified as one of the major chemical lump such as alkanes, phenols and aromatics are lumped together as unidentified. The addition of the ms to our system will enable identification of these species. However, the species in this lump include saturated and unsaturated cycloalkanes with or without side chains, which resembles the naphthenes, a petroleum refinery product group. A number of well known species in coal liquid are not mentioned in this lumping scheme. Such as heterocyclic compounds with sulfur, nitrogen or oxygen as the hetero atom, and other hetero atoms containing species. Some of these compounds appear with aromatics (eg. thiophenes, quinolines) and with phenols (eg. aromatic amines), and most of them are lumped with the unidentified species lump.

Since SEC-GC can be equipped with a number of specific detectors such as nitrogen specific detector (TSD), flame photometric detector for sulfur (FPD) and mass spectrometer, the lumping of chemical species can be performed for any selected group of species such as polycyclic aromatics, thiophenes and nitrogen species.

Conclusions

Although SEC and GC are two powerful chromatographic techniques, their combined use for analyzing complex mitures has been limited due to the time consuming steps involved. The two valve interface which links the liquid chromatograph to gas chromatograph and the computer system which automate the system, reduce the analysis time as well as the frequency of manual interaction during the analysis which may take 8-10 hours for a coal liquid sample. By adding a mass spectrometer as a third detector to the GC, an extensive analysis of a rather complex sample such as coal liquid, petroleum crude and their refinery products can be achieved.

With the help of additional devices such as MS, SEC-GC is not expected to identify all the components of coal liquids. It may very well be true that all the positively identified components may represent only a fraction of all the components

and the mass fractions of all the identified species may very well represent only a minor fraction of the coal liquid. But the lumping of chemical species into fewer groups will be for the whole sample and the chemical nature of large number of species which are not totally identified are recognized for their structure based on similarity on of functional groups or main structural block. The lumping of chemical species as shown in Figure 14 is a good approximation which needs varification by detailed analysis.

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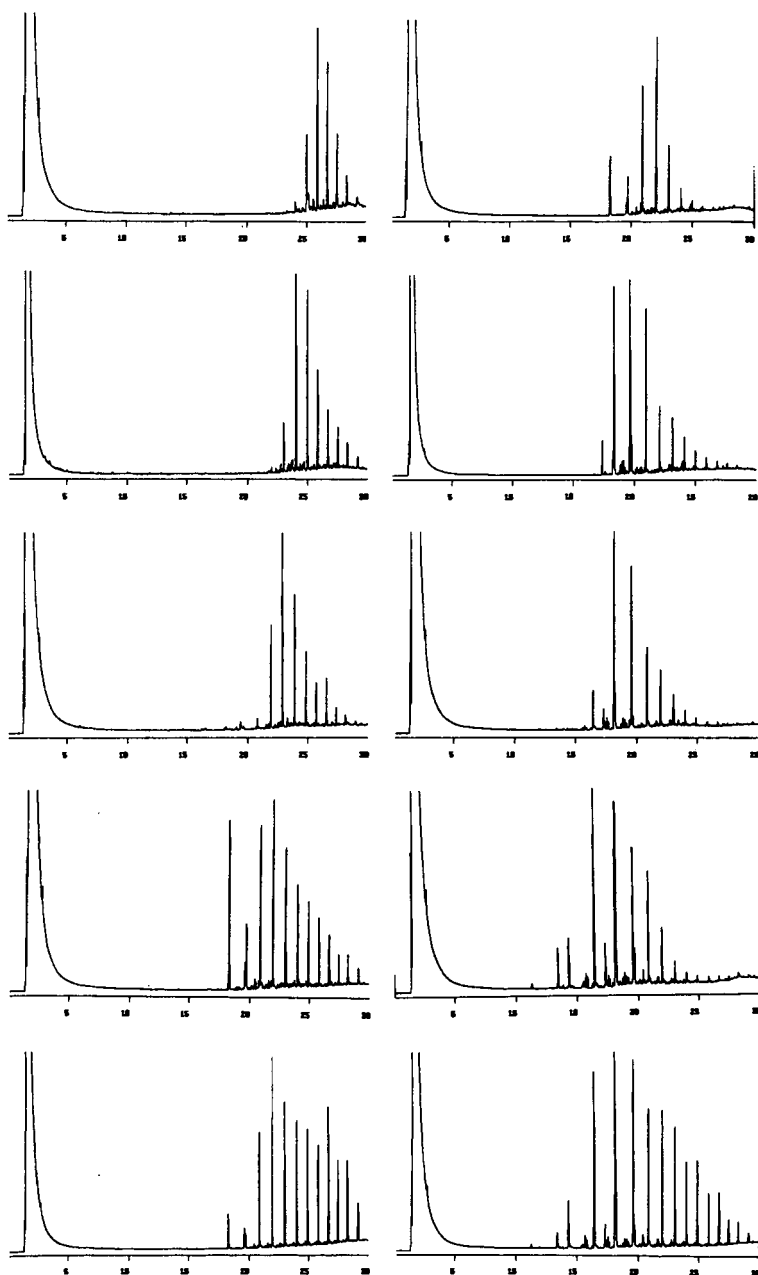
Figure 3:   The effect of column overloading by alkanes of coal liquids.
             Top to bottom: 20 mg synthoil, 50 mg synthoil, 50 mg ZAP
             recycle solvent, 50 mg Texas Big Brown recycle solvent, 50
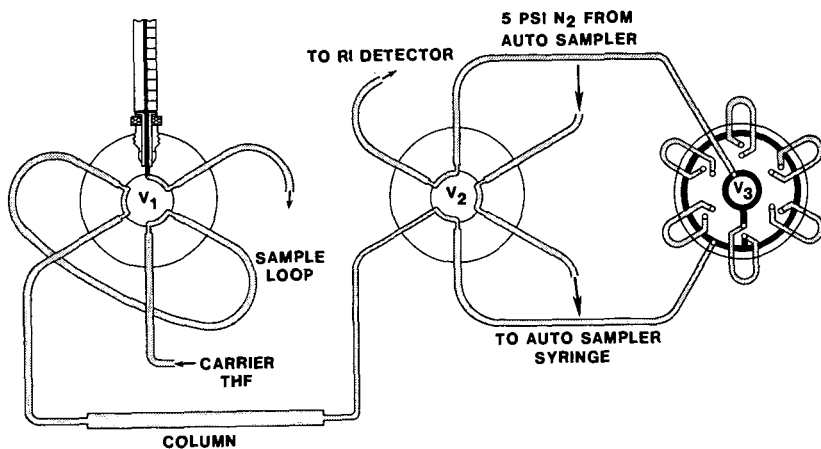   mg Wyodak recycle solvent.

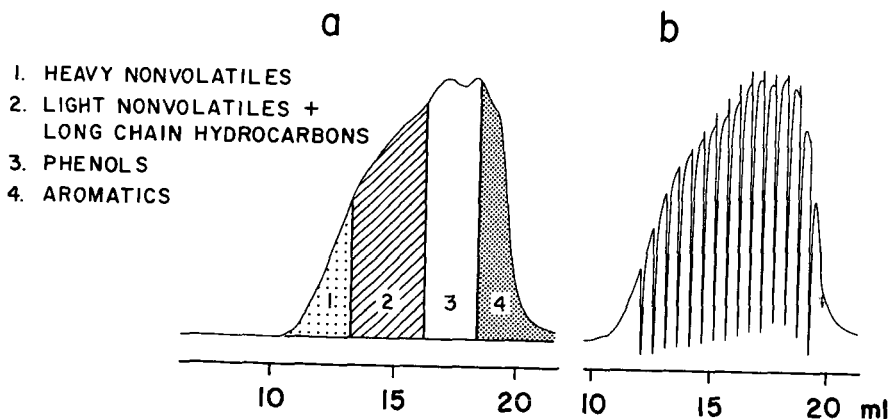Figure 1: SEC-GC interface. Note: V_3 has sixteen loops instead of six.

1. HEAVY NONVOLATILES
2. LIGHT NONVOLATILES +
   LONG CHAIN HYDROCARBONS
3. PHENOLS
4. AROMATICS

Figure 2: SEC separation of Wydak coal derived recycle solvent (1) SEC-GC interface bypassed (b) 16 fraction were collected by SEC-GC interface.
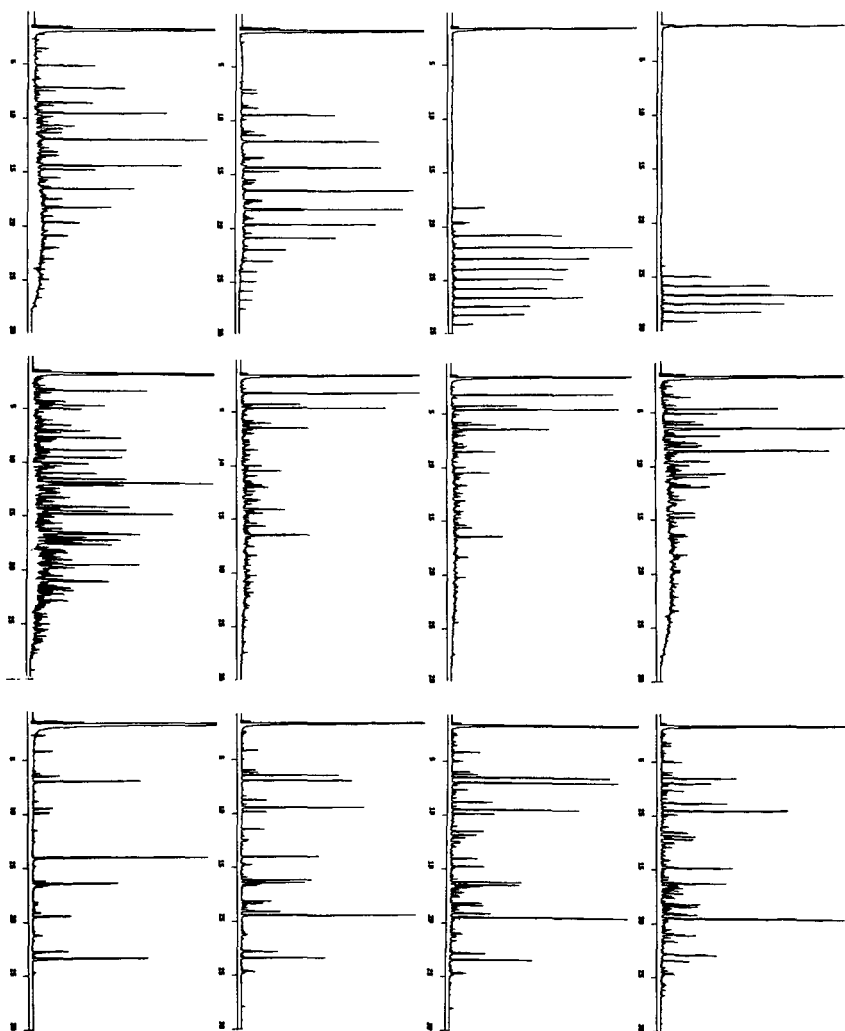
Figure 4: Gas chromatograms of SEC fractions from Wyodak recycle solvent. Base lin subtraction
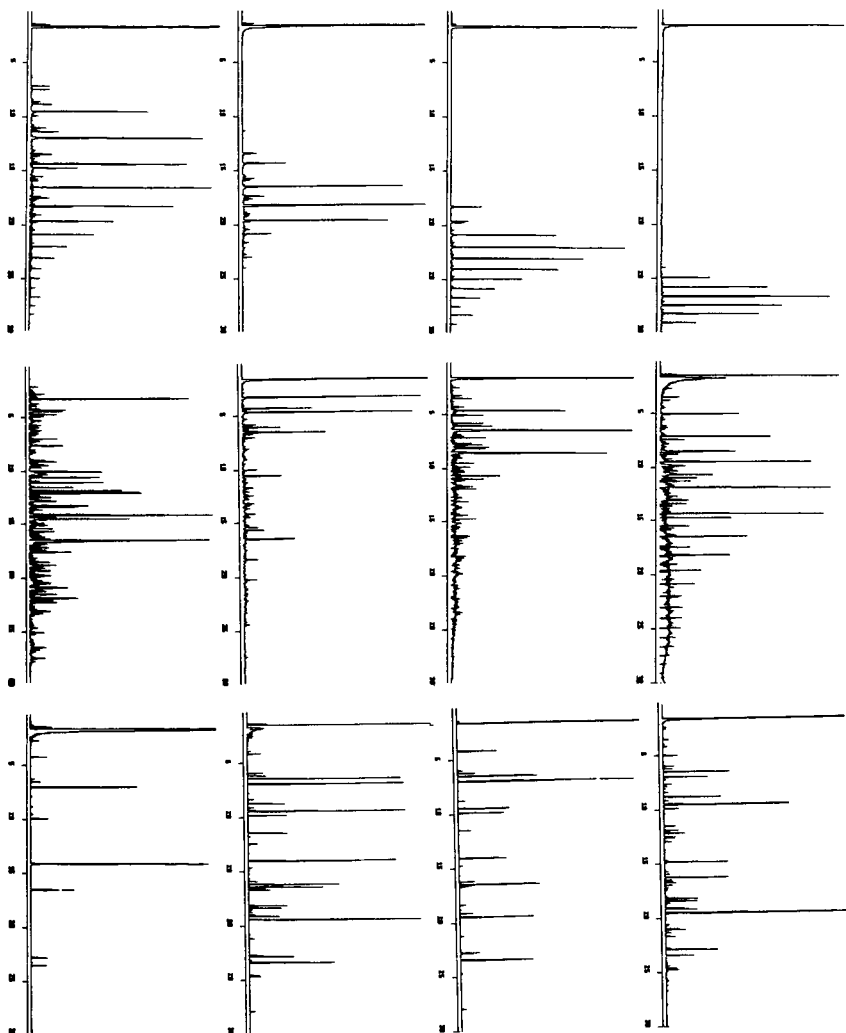
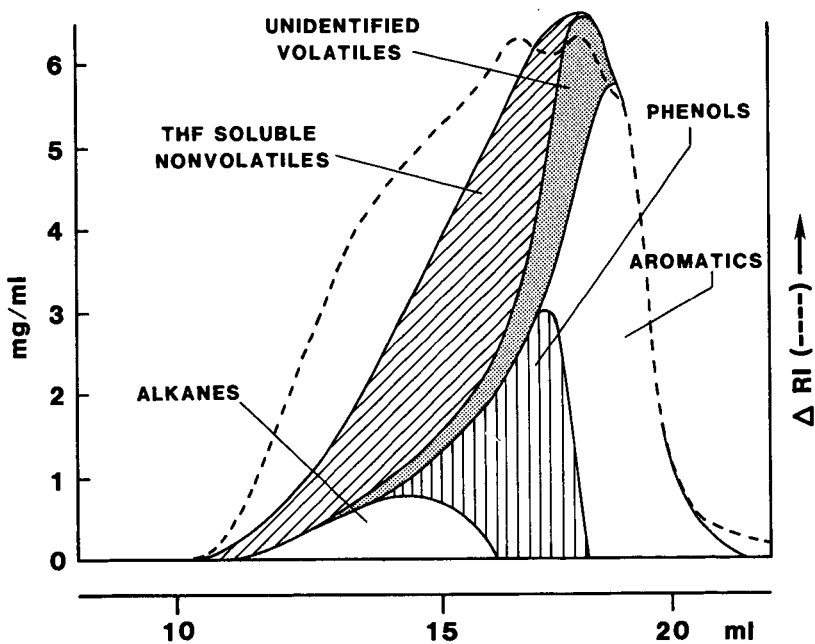Figure 5: Reconstructed gas chromatogram showing only new peaks

Figure 6:   Lumping of chemical species in Wyodak recycle solvent.